

ATMOSPHERIC TRANSPORT, TRANSFORMATION, AND DEPOSITION OF MERCURY IN THE NORTHEASTERN UNITED STATES

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INTRODUCTION

The health risks associated with consumption of mercury contaminated fish are a widespread concern. It is generally believed that the atmospheric deposition of mercury is a major source of the observed elevated concentrations of mercury in fish. Atmospheric deposition is therefore directly related to mercury-based health concerns, but is a problem that cannot be addressed locally. Because of the complexity of the Hg cycle that involves the atmosphere, geosphere, and biosphere, Hg must be viewed in either a regional or global scale. This is particularly important due to its long atmospheric lifetime and ability to re-enter the atmosphere. In this study, methods described in Xu (1998) and Xu et al. (1999) were used to estimate the atmosphere-surface exchange of elemental Hg including emission and dry deposition. In this model, atmospheric transport and transformation of mercury were incorporated into a three-dimensional Eulerian air quality model that included soot and ozone and was fully coupled to in-cloud processes. The model was used to predict Hg concentration and deposition in the northeastern United States for one summer and one winter week during 1997. Additional simulations were also conducted to study the sensitivity of regional Hg deposition to the partitioning of Hg(II) between particulate and non-particulate forms.

MODEL DEVELOPMENT

The atmospheric transport and transformations of mercury were incorporated into SAQM (Sarmap Air Quality Model, Chang et al. 1987; 1996), a three-dimensional regional scale air quality model. A one-dimensional cloud module based on Chang et al. (1987), Dennis et al. (1993) and Tsai (1996) was incorporated into SAQM. Three mercury species were considered: elemental [Hg(0)], divalent [Hg(II)], and particulate [Hg(p)]. Soot particles were also considered. The major aqueous chemical processes included oxidation of dissolved Hg(0) by ozone, reduction of Hg(II) by sulfite, and adsorption of Hg(II) onto soot particles. The aqueous phase chemical reactions largely followed Petersen et al. (1995), but included three types of clouds: precipitating, co-existing non-precipitating, and fair weather clouds. The interaction between the in-cloud transformation of Hg(0) and direct scavenging of ambient Hg(II) was also considered. The air-surface exchange of Hg(0) was treated by explicitly considering both dry deposition and re-emission from bare soil, vegetation, and water surfaces (Xu et al., 1999).

Simulation periods and domain

Simulations were conducted for two weeks during the year 1997. The winter week simulation started at 1900 hours eastern standard time (EST) on Feb. 13 1997 and lasted 96 hours. For the summer week, the simulation started at 1900 EST on Aug. 20 1997 and lasted 120 hours. The domain of the simulation covered the northeastern U.S. and part of the Atlantic Ocean as shown in Fig. 1. Grid spacing considered 34×41 grids in the horizontal direction, with grid size of $12 \text{ km} \times 12 \text{ km}$, and 15 layers in the vertical direction with the center of the lowest layer located approximately 30 m above the ground. The top of the modeling domain was approximately 15.5 km. Meteorological data were taken from Pennsylvania State University (PSU), generated by the PSU/NCAR (National Center for Atmospheric Research) Mesoscale Model, Version 5 (MM5). The regional average precipitation predicted by MM5 was 4.67 cm and 1.94 cm for the summer and winter week, respectively.

Model input for the base case simulations

A baseline simulation was conducted using measured or estimated concentrations for the major pollutants. Hourly ozone concentrations were taken from near-surface measurements in the USEPA (United States Environmental Protection Agency) database with horizontal and vertical interpolation. Ambient soot concentrations were estimated from ozone and $\text{PM}_{2.5}$ measurements by the USEPA. Mercury emissions from combustion sources in Connecticut (CT) were provided by the Connecticut Department of Environmental Protection (CTDEP). Anthropogenic Hg emissions from other parts of the modeling domain were based on the USEPA study (USEPA, 1996). Speciation of Hg from combustion sources followed Petersen et al. (1995). Mercury

initial and boundary concentrations were set at 1.3 ng/m^3 for $\text{Hg}(0)$, and 0.01 ng/m^3 for each of $\text{Hg}(\text{II})$ and $\text{Hg}(\text{p})$.

Sensitivity simulations

Additional simulations were conducted by changing the speciation of Hg emission from anthropogenic sources or including adsorption of $\text{Hg}(\text{II})$ onto soot particles. The alternative emission speciation assumed all $\text{Hg}(\text{II})$ emissions were attached to particles. For the partitioning between ambient $\text{Hg}(\text{II})$ and $\text{Hg}(\text{p})$, an adsorption coefficient of $K = 3 \times 10^9 \times [\text{soot}]$ was adopted from Seigneur et al. (1998).

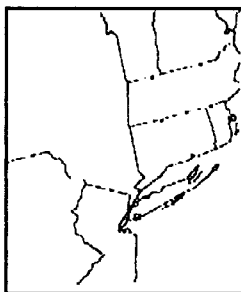


Figure 1. The domain of simulation.

Data analysis

For the baseline runs, the predicted weekly average ambient Hg concentrations and Hg concentrations in precipitation in CT were compared with weekly observations conducted by CTDEP and The University of Connecticut Environmental Research Institute (ERI). For comparing the sensitivity simulation results with those in the base case, the normalized deposition rates were calculated and presented by dividing the predicted regional daily average dry, wet, and total deposition with the corresponding value of the base case.

RESULTS AND DISCUSSION

Modeling results (base case) in comparison with monitoring data

Fig. 2 compares the model estimated summer week ambient concentrations of gaseous Hg [$\text{Hg}(0) + \text{Hg}(\text{II})$] and $\text{Hg}(\text{p})$ with measured values at eight monitoring stations in CT during the same time period. For gaseous Hg, the model was able to recapture the spatial variation as observed by the monitoring stations. The modeled values agreed well with monitoring data except at site WB where the measured Hg concentration was higher than at all other sites, for that week and throughout the year of 1997 (ERI, 1998). There are two possible reasons for the underprediction by the model at WB: the exclusion of several undocumented Hg emission sources in the emission inventory, or the location of the monitoring site too close to these or other local Hg sources.

The model overpredicted the ambient $\text{Hg}(\text{p})$ concentration at all eight monitoring sites (Fig. 2b). The modeled values were also higher than $\text{Hg}(\text{p})$ concentrations measured in other regions, which ranged from 0.011 ng/m^3 in Underhill Center, VT (Burke et al., 1995) to 0.094 ng/m^3 in Detroit, MI (Keeler et al., 1995). This might have reflected the limitation of the model in handling the broad distribution of particle sizes. Because the largest particles will be poorly mixed and will deposit close to the stack, it is likely that the model would underestimate dry deposition and hence overestimate ambient concentrations of $\text{Hg}(\text{p})$.

The predicted summer week precipitation results agreed reasonable well with measurements (Fig. 3a). The modeled total Hg concentrations in precipitation, ranging from 7.68 to 11.7 ng/l , were higher than observations in general, as shown in Fig. 3b. The model estimates were comparable with published measurements (e.g. Fitzgerald et al., 1991; Rea et al., 1996; Keeler and Hoyer, 1997).

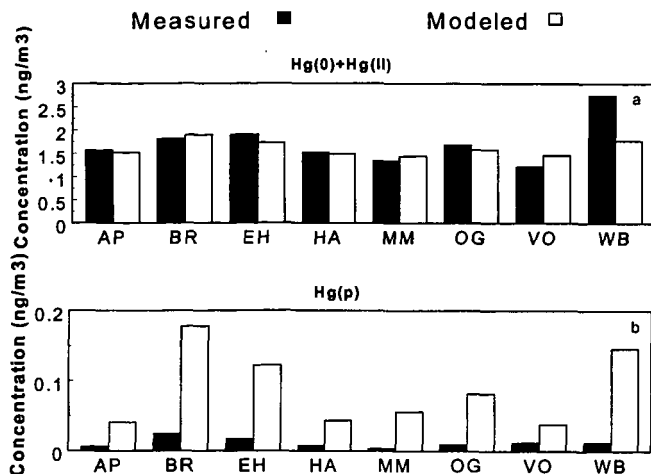


Figure 2. Comparison of modeled gaseous Hg concentrations (a) and Hg(p) concentrations (b) with monitored values in CT stations, during the summer week simulation. AP-Avery Point, BR-Bridgeport, EH-East Hartford, HA-Hammonasset, MM-Mohawk Mountain, OG-Old Greenwich, VO-Voluntown, WB-Waterbury.

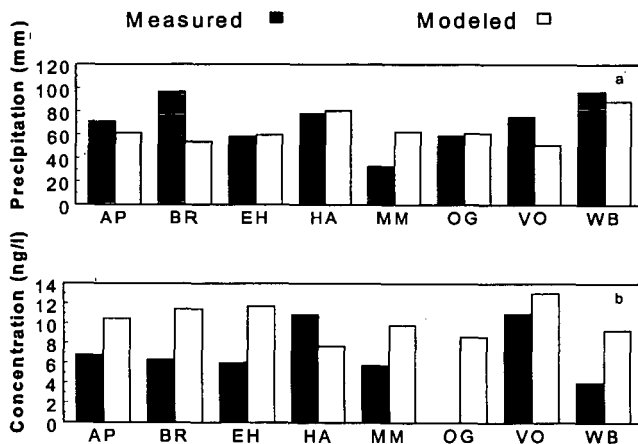


Figure 3. Comparison of modeled weekly precipitation (a) and Hg concentrations in precipitation (b) with monitored values in CT stations, during the summer week simulation. Concentration measurement was not available at OG.

The comparison between winter week simulation and measurements was similar to that of the summer week, with good agreement in gaseous concentration and precipitation concentration, but overprediction of ambient Hg(p) concentration.

Effects of emission speciation and Hg(II) adsorption to soot on Hg deposition

Table 1 lists normalized wet, dry, and total deposition of the region for the summer and winter week. By assuming all Hg(II) emissions were attached to particles, the ambient concentrations of Hg(p) increased, and concentrations of Hg(II) decreased. There was a significant decrease in dry deposition of Hg(II), but a large increase in the dry deposition of Hg(p). The total dry deposition decreased dramatically. This is because the dry deposition velocity of Hg(p) was much lower than that of Hg(II). The total wet deposition increased over the base case, as reported by Bullock et al. (1997), primarily due to a significant increase in wet deposition of Hg(p) and Hg(0). The resulting total deposition was less than in the base case.

When Hg(II) adsorption to soot particles was considered, the resulting partitioning between ambient Hg(II) and Hg(p) caused a decrease in the dry deposition of Hg(II) and an increase in the dry deposition of Hg(p), but to a lesser extent than in the case of alternative emission speciation. Similarly, the gas phase partitioning led to less wet deposition of Hg(II), and more wet deposition of Hg(p) and Hg(0). Compared with the alternative emission speciation, the Hg(II) adsorption to particles resulted in less reduction of total deposition because the alternative emission speciation influenced heavily concentrations near the surface where point sources were located. Thus, Hg(II) dry deposition was largely reduced, leading to much lower dry deposition.

As can be seen from Table 1, deposition during the winter was more sensitive to changes in ambient Hg(II) concentration compared with the summer week. This can be largely attributed to the different Hg species that predominate the deposition during warm and cold seasons. In the winter week, approximately 65% of total deposition was from Hg(II), in comparison with 40% in the summer week.

Table 1. Normalized regional deposition from model simulation during the summer and winter weeks.

Simulation	Summer			Winter		
	Dry dep.	Wet dep.	Total	Dry dep.	Wet dep.	Total
Alternative emission speciation	0.57	1.14	0.76	0.27	1.19	0.52
Adsorption of Hg(II) to soot, gas phase	0.78	1.10	0.89	0.48	1.16	0.67

SUMMARY AND CONCLUSIONS

Model predictions of surface level gaseous Hg concentrations were close to measured levels, agreeing to within 12% on average, about half the estimated error in measurements. The predicted Hg concentrations in precipitation were 50% higher than measured values on average, slight lower than the estimated 60% error in measurements. The modeled ambient particulate Hg concentrations, on the other hand, were much higher than measurements made in CT and other places, suggesting an underestimation of dry deposition in the source grids.

Both the alternative emission speciation and the adsorption of ambient Hg(II) onto soot particles resulted in less total deposition of Hg, indicating the dependence of total deposition on the fraction of gaseous mercury bound to particles. It is therefore important to determine accurately the emission speciation and transformation during transport.

In conclusion, the model was shown to be capable of producing acceptable results, and useful in analyzing the effects of various environmental factors on the atmospheric transport, transformation, and deposition of Hg. More simulations to address seasonal variations and to further evaluate the model are being conducted.

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